

3900

SYMPOSIUM: SWEETENERS

Edited by

George E. Inglett, Ph.D.
*Chief, Cereal Properties
Laboratory, Northern Regional
Research Laboratory, ARS, USDA,
Peoria, Illinois*

Maple syrup and honey are sweeteners with much in common. Each has origins obscured in history, each has served as a principal sweetener in the past, and the increasing cost of each has greatly reduced their importance as basic sweeteners in favor of their role as flavorants.

Otherwise, they differ in nearly every respect. Maple syrup is man-made from maple sap, derives its flavor from heat-induced reactions, is essentially a flavored, saturated sucrose solution, and is produced only in the U.S. and Canada. Honey, of course, is a natural product, produced by the honeybee from the nectar of flowers, is ready to be consumed as produced, is essentially a fructose solution supersaturated with glucose, and is a world commodity.

MAPLE SYRUP

When the white man settled in the northeastern section of what is now the U.S. and nearby Canada, he found the American Indian making maple syrup and sugar. The discovery of the secret of the sugar maple tree is shrouded in history, but many nostalgic tales describe the event (Nearing 1950). The Indians had various names for it: *sinzibuckwud* (drawn from the wood—Algonquin); *sheesheegummawis* (sap flows fast—Ojibway) and *sisibaskwat* (Cree). Whatever its origin, many settlers quickly recognized the value of maple sugar and learned to make it themselves. However, the product did not become a significant part of the diet in the colonies until the beginning of the eighteenth century when tea and coffee became social beverages (Fox 1905; Raymond 1969). This development brought with it the use of sugar as a sweetener. Since cane sugar was expensive and often very difficult to obtain, the settlers in the Northeast produced and used maple sugar.

The position of West Indies cane sugar in Colonial trade and its taxation greatly increased interest in production of maple sugar. Disruption of sugar trade during and after the Revolution, together with settling of areas west of the original colonies, increased maple sugar production during the 19th century to a maximum of 6 to 6.5 million gal (syrup equivalent) in 1880-1890. During this time, Canadian production increased to over 3 million gal.

TABLE 10.1
PRODUCTION OF MAPLE SYRUP IN UNITED STATES AND CANADA¹

Year	United States Thousand Gallons (US)	Canada Thousand Gallons (US)
1850	4,282	—
1860	6,613	—
1870	4,477	2,160
1880	6,368	2,570
1890	6,377	3,136
1900	3,548	2,226
1909	5,859	3,476
1919	4,719	3,014
1929	2,509	2,385
1939	2,501	2,616
1949	1,480	2,608
1959	1,049	3,092
1971	962 ²	—

¹ Raymond and Winch 1969.

² USDA 1972.

Since 1900, domestic production of maple sugar and syrup has declined as the supply of other sugars—cane, beet, corn—has increased (Table 10.1). As the market price of these commodities fell far below that of maple sugar, the demand for maple sugar became related to its unique flavor, and consumer preference changed to the syrup, 97 to 98% now being sold in this form. Since 1950 maple syrup production in the U.S. had fluctuated between 1 and 1.5 million gal. The most important maple syrup-producing states in decreasing order are (1968 to 1971) New York, Vermont, Ohio, Pennsylvania, Michigan, Wisconsin, New Hampshire, Massachusetts, Maine, and Minnesota. Canadian production, about 3 million gal (US) by 1890, has remained near this level, and the U.S. imports about half of this. With below-average crops in 1969, 1970, and 1971 due to environmental factors which regulate sap flow, the maple syrup producer now faces the possibility that continued short supply and high prices will force large commercial users to seek substitutes.

Making Maple Syrup and Sugar

According to Federal Standards (USDA 1940) "maple syrup" means syrup made by the evaporation of maple sap or by the solution of "maple concrete" (maple sugar). The latter is a form of maple sugar made by concentrating the maple sap far beyond the saturation concentration of the sugar, to about 92% solids. When this hot liquid cools, the sugar crystallizes into a mass for which the term

concrete is well-suited. In 50-lb cakes this was a convenient form to store maple syrup. It is too hard for a confection and difficult to redissolve on a small scale. Very little maple concrete is now produced because improved means of storing the syrup have been developed.

The operations involved in collecting the maple sap (known to many farmer-producers as "sweet water") early in the spring and boiling it down to syrup have changed considerably since 1900. No longer, except as a tourist attraction, do we see producers emptying sap-collecting buckets into tanks on horse-drawn sledges and boiling the sap down in an open flat pan over a roaring wood fire in a makeshift lean-to sugarhouse. Today (Underwood and Willits 1963) the modernized maple syrup producer conducts his operations in a stand of sugar maple trees (sugar bush) that has been tree-managed to give him trees spaced properly for vigorous growth and optimum access for sap collection. The trees are tapped with a power drill to a depth of 3 in. and an antiseptic tablet and a plastic "spile" are inserted. When a tree attains a diameter of 10 in. it can support one taphole. For each additional 5 in. another hole may be drilled. To collect the sap, the tapholes are connected into a plastic tubing system which drains into collection tanks or directly into a storage tank at the evaporation plant (sugar house). Where appropriate, vacuum pumping systems are now being installed in plastic tubing collection systems to aid the flow of sap in the lines and even to increase the yield of sap from the tree.

In an enclosed building (sugar house) with a solid floor the sap is evaporated in open, flat pans by atmospheric boiling to a sugar concentration of 65.5% by weight, the minimum concentration in syrup that meets Federal and State specifications. The characteristic maple flavor and color are developed during the evaporation process, which involves exposure to temperatures above 100°C. If the evaporation is done by freeze-drying or under vacuum, only a colorless, flavorless syrup is produced. In other words, flavor and color are not characteristics of the sap as it emerges from the tree, but are developed by the heat applied during concentration. Processing conditions have been established to optimize the production of the light-colored, most distinctively maple-flavored syrups, which bring the highest prices on the retail market. The flat-pan evaporator is efficient (Strolle 1963) and well suited to the making of maple syrup, especially for the small-volume operation usual in the maple industry. It is now being complemented by modern accessories for better control of processing factors. These include the substitution of oil or high-pressure steam for wood as the heat source to obtain a steady maximum rate of evaporation.

Instruments have been developed or adapted for precise control of the end point of evaporation. Standard density syrup (65.5% sugar by weight) boils at 7°F above the boiling point of water at any barometric pressure. Special thermometers are now used for maple sap evaporators that relate syrup temperatures to sugar concentration. Automatic valves withdraw syrup from the evaporator at any desired point of evaporation (Connelly 1969). The flat-pan evaporator is now provided with a tight-fitting cover with a stack for removing steam from the sugar house. This venting system is essential to sanitary operation since it not only keeps foreign materials out of the boiling sap, but also produces a warm, steam-free sugar house. Sanitary practices can now be followed, as in other food-processing plants.

Most maple syrup is still produced by small, individual farm family enterprises. However, centralized sap processing plants are now developing throughout the maple industry, sap collection and evaporation to syrup becoming two separate operations. Improved sap preservation by ultraviolet irradiation has made this practical. Only a limited capital investment and a minimum of labor are needed to put a "sugar bush" into operation and to harvest sap. The central plant can concentrate on making syrup and other maple products and consequently operate on a larger scale. With more syrup, the central plant can do a better job in marketing. A comprehensive description of the new technology is available (Willits 1965).

Composition of Maple Syrup

Maple sap as it exudes from the tree is sterile, and the solids content (usually 2 to 3%) is essentially sucrose, free of reducing hexoses. About 3% of the solids is a mixture of organic acid salts (calcium malate predominating), traces of nitrogen-containing material, a lignin-like substance, and other carbohydrates. If the sap can be reduced to syrup with minimum change in the sucrose, a light-colored, delicately flavored syrup results (Edson 1912; Hayward and Pederson 1946). However, poor-quality sap and/or faulty processing techniques can produce darker, stronger-flavored syrups. Since the syrups with distinct maple flavor and without acrid "caramel" flavor are lighter in color and command higher prices in the market, color is the principal grading factor. Standards have been set by the USDA for interstate commerce (USDA 1940) and by the various states for local sale. Other characteristics, such as density, flavor, and clarity are also considered. The Federal, New York, and Vermont grade designations are listed in Table 10.2.

Chemically, the various grades of maple syrup do not differ except in content of the reducing sugars glucose and fructose, which

TABLE 10.2

GRADE DESIGNATIONS OF MAPLE SYRUP, AS DETERMINED BY COLOR¹

Grade Designation	Color	Color Index Range ²
US Grade AA New York Fancy Vermont Fancy	As light as or lighter than Light Amber ³	0 — 0.510
US Grade A New York No. 1 Vermont A	Darker than Light Amber but as light as or lighter than Medium Amber ³	0.510 — 0.897
US Grade B New York No. 2 Vermont B	Darker than Medium Amber and as light as or lighter than Dark Amber ³	0.897 — 1.455
US Unclassified New York No. 3 Vermont C	Darker than Dark Amber	Over 1.45

¹ Willits 1965.² Color index = $A \frac{86.3\%}{1 \text{ cm}} = A_{450} (86.3/bc)$ A_{450} is the absorbance at 450 nm with distilled water used as a blank; b is depth of solution in cm; and c is gm of solids as sucrose per 100 ml of solution.³ The terms Light, Medium, and Dark Amber refer to standard glass color filters in the USDA maple syrup color classifier.

TABLE 10.3

COMPOSITION OF MAPLE SYRUP¹

Component	Amount %	Component	Amount %
Water	34.0	Soluble ash	0.30-0.81
Sucrose	58.2-65.5	Insoluble ash	0.08-0.67
Hexoses	0.0-7.9	Calcium	0.07
Malic acid	0.093	Silica	0.02
Citric acid	0.010	Manganese	0.005
Succinic acid	0.008	Sodium	0.003
Fumaric acid	0.004		

¹ Willits 1965; Hart and Fisher 1971.

increases as the color in the syrup increases, but does not change the sweetening power of the product significantly. A typical composition of maple syrup is shown in Table 10.3. Maple syrup, like other table syrups, has no special nutritive value other than to provide calories. All of them are used primarily to satisfy man's craving for sweet-tasting foods.

In the stiff competition among the many different types and brands of table syrups marketed, consumer preference is generally

wooed by the flavor of the particular syrup, and maple syrup meets this competition very well. The true gourmet prefers pure maple syrup to all other table syrups. Most consumers have probably never tasted pure maple syrup. This makes even more startling the overwhelming preference for maple-flavor syrups by the average consumer. A survey conducted by the Homemakers Guild of America (1961) showed that 55% of the consumers contacted preferred maple syrup, 15% corn syrup, 6.6% cane syrup, and 23.1% had no preference. However, pure maple syrup is expensive and most consumers feel they cannot afford this product for daily use. But, because the competition among the national brand table syrups is so great, many companies use the selling power of the maple flavor by marketing products flavored with low percentages of pure maple syrup and/or artificial flavorants resembling maple.

It is clear that the flavorants are now the most important components of maple syrup. Certainly, all the components of maple syrup contribute to its flavor—the sugar, the organic acid salts, and even the oil, butter, or whatever has been used as an antifoam agent during evaporation. However, there is an unknown number of trace materials in the syrup or sugar that gives it “maple flavor”. Because these are present in parts per million, they had defied identification for many years, but now, with the modern techniques of gas chromatography and mass spectrometry, progress is being made in solving the mystery of “maple flavor”. The flavorants identified to date can be divided (Filipic *et al.* 1969; Underwood 1971) into two groups according to their probable source. One group, possibly formed from ligneous materials in the sap, contains such compounds as vanillin, syringaldehyde, dihydroconiferyl alcohol, acetovanillone, ethylvanillin, and guaiacyl acetone. A second group, most likely formed by caramelization of the carbohydrates in the sap, includes acetol, methylcyclopentenolone (cyclotene), furfural, hydroxymethylfurfural, isomaltol, and alpha-furanone.

Uses of Maple Syrup and Maple Sugar

The most direct use of maple syrup or sugar, aside from pure maple syrup or in blends, is in the production of pure maple confections. There are several products worth mentioning as examples of the general types of products. The maple sugar cake is the easiest to make and is the most popular maple confection. This is a small-crystal soft- or hard-textured product made in many forms. Another popular item is a spread called maple cream or maple butter; properly made, it has the consistency of peanut butter and is delicious on toast or crackers. Unfortunately, this product has an

uncertain shelf life due to separation of the solid and liquid phases which has limited this really delightful confection to markets local to the producer. A third product containing only maple syrup is crumb sugar, or stirred sugar. This is a granulated sugar product made by boiling syrup to the correct degree of supersaturation and allowing it to crystallize with stirring. Many special variations of these general types are made by enterprising maple products farmers. Details about these can be obtained from the Experiment Stations in the states where the maple industry is active.

Both maple syrup and sugar are used in many foods because of their flavor contributions. Some users have the opinion that maple syrup or sugar is a flavor enhancer, i.e., the effect of certain original flavorants in foods is increased by the addition of maple syrup. Can this be related to its content of methylcyclopentelone, a material now being promoted as a flavor enhancer? Among the food preparations in which maple syrup or sugar are used as an ingredient are cookies, cakes, cake icings, baked beans, candies, ice cream, baked ham, candied sweet potatoes, baked apples, and fresh grapefruit. Recipes for the use of maple in food preparation are available from the Extension Services of many universities and at sales outlets for maple products.

It has been pointed out that maple sugar, since its development as a sweetener during the Revolution, has lost a competitive economic race to cane and beet sugar. However, the American people like maple flavor, and maple syrup continues to be sought by the gourmet. The industry remains small due to the climatic limitations of hard maple growth, the flow of maple sap, and the weather conditions under which maple sap is collected and made into syrup. But perhaps the present growing interest in the use of natural foods may stimulate an increase in the production of maple products.

HONEY

Honey is the sweet viscous fluid elaborated by bees from nectar obtained from plant nectaries, chiefly floral. After carrying it to the hive, the bee ripens this fluid and stores it in the comb for food. "Ripening" is inversion of nectar sucrose and simultaneous concentration of the nectar to about 82% solids. The U.S. Food and Drug advisory definition for honey states that "Honey is the nectar and saccharine exudation of plants, gathered, modified, and stored in the comb by honeybees (*Apis mellifera* and *A. dorsata*); is levorotatory; contains not more than 25% water, not more than 0.25% ash, and not more than 8% sucrose". Although this definition once served a useful purpose, it is considered today to allow much too high a

content of water and sucrose and is too low in ash (White *et al.* 1962).

The general characteristics of honey—its sugar composition, color, and flavor—depend upon the kinds of flowers from which it is made by the honeybee. Honey color may vary greatly, from a nearly colorless fireweed or sweetclover type through yellow, yellow green, gold, ambers, dark browns or red browns to the nearly black buckwheat honey. The variations are almost entirely due to the plant source of the honey, though climate may modify the color somewhat by the darkening action of heat.

The flavor of honey also varies over a wide range. A honey may appear to have only a simple sweetness or may be mild, spicy, fragrant, aromatic, bitter, harsh, medicinal, or very objectionable. This is again almost entirely governed by the floral source. In general, a light-colored honey is expected to be mild in flavor and a darker honey to be of pronounced flavor. The exceptions common to all rules sometimes endow a light honey with very definite specific flavors.

Honey is doubtless the oldest sweet known to man, having been the principal sweetener before the discovery of cane sugar. It is probably the only commercially important sweetening material that requires no processing before consumption. For successful handling in commerce, however, it is commonly heated to destroy yeasts and to delay granulation, and generally is either strained or filtered to remove extraneous materials.

About 200 to 250 million lb are produced annually in the U.S. and 15 to 35 million more are imported, largely from Mexico, Argentina, Canada, and Australia. Recent consumer interest in "organic" and natural foods and increases in Japanese imports, together with short crops, have created shortages and prices have doubled since early 1971.

Composition of Honey

The characteristic physical properties of honey—high viscosity, 'stickiness', great sweetness, relatively high density, tendency to absorb moisture from air, and immunity to some types of spoilage—all arise from the fact that natural honey is a very concentrated solution of several sugars. Because of its unique character and its considerable difference from other sweeteners, chemists have long been interested in its composition, and food technologists sometimes have been frustrated in attempts to include honey in prepared food formulas or products.

Average Composition and Variability.—In an analytical survey of U.S. honey (White *et al.* 1962), considerable effort was made to

obtain honey samples from all over the U.S. and to include enough samples of the commercially significant floral types that the results, averaged by floral type, would be useful to the beekeeper and packer and also to the food technologist.

The bulletin includes complete analyses of 490 samples of U.S. floral honey and 14 samples of honeydew honey gathered from 47 of the 50 states and representing 82 "single" floral types and 93 blends of "known" composition. For the more common honey types, many samples were available and averages were calculated for many floral types and plant families. Detailed discussions of the effects of crop year, storage, area of production, granulation, and color on composition are included. Some of the tabular data are included here.

Table 10.4 gives the average and the range of values found for each component (White *et al.* 1962).

TABLE 10.4
AVERAGE COMPOSITION OF US HONEY AND RANGE OF VALUES¹

Characteristic or constituent		Floral Honey	
		Average values	Range of Values
Color ²		Dark half of white	Light half of water white to dark
Granulating tendency ³		Few clumps of crystals, 1/8- to 1/4-inch layer	Liquid to complete hard granulation
Moisture	percent	17.2	13.4 - 22.9
Fructose	"	38.19	27.45 - 44.26
Glucose	"	31.28	22.03 - 40.75
Sucrose	"	1.31	0.25 - 7.57
"Maltose" ⁴	"	7.31	2.74 - 15.98
Higher sugars	"	1.50	0.13 - 8.49
Undetermined	"	3.1	0 - 13.2
pH		3.91	3.42 - 6.10
Free acidity ⁵		22.03	6.75 - 47.19
Lactone ⁵		7.11	0 - 18.76
Total acidity ⁵		29.12	8.68 - 59.49
Lactone ÷ free acid		0.335	0 - 0.950
Ash	percent	0.169	0.02 - 1.028
Nitrogen	"	0.041	0 - 0.133
Diastase ⁶ (270 samples)		20.8	2.1 - 61.2

¹ Based on 490 samples of floral honey.

² Expressed in terms of USDA color classes.

³ Extent of granulation for heated samples after 6 months' undisturbed storage.

⁴ Reducing disaccharides as maltose.

⁵ Milliequivalent per kilogram.

⁶ Grams of starch converted by enzyme in 100 gm honey in 1 hr under assay conditions.

The carbohydrate composition of the more common types of honey is shown in Table 10.5. In all cases fructose predominates, although there are a few types, not represented in the table, that contain more glucose than fructose, such as dandelion and bluecurls. This typical excess of fructose over glucose is one way that honey differs from commercial invert sugar. Although honey has less glucose than fructose, the former is the sugar that crystallizes when honey granulates or "sugars". The sucrose level in honey never reaches zero, even though it may contain an active sucrose-splitting enzyme.

The principal physical characteristics and behavior of honey are due to its sugars, but the minor components, such as flavoring

TABLE 10.5

CARBOHYDRATE COMPOSITION OF COMMERCIALY IMPORTANT HONEY TYPES

No. of Samples	Floral Type	Glucose	Fructose	Sucrose	"Maltose"	Higher Sugars
		%	%	%	%	%
23	Alfalfa	33.40	39.11	2.64	6.01	0.89
25	Alfalfa-sweetclover	33.57	39.29	2.00	6.30	0.91
5	Aster	31.33	37.55	0.81	8.45	1.04
3	Basswood	31.59	37.88	1.20	6.86	1.44
3	Blackberry	25.94	37.64	1.27	11.33	2.50
5	Buckwheat	29.46	35.30	0.78	7.63	2.27
4	Buckwheat, wild	30.50	39.72	0.79	7.21	0.83
26	"Clover"	32.22	37.84	1.44	6.60	1.39
3	Clover, alsike	30.72	39.18	1.40	7.46	1.55
3	Clover, crimson	30.87	38.21	0.91	8.59	1.63
3	Clover, Hubam	33.42	38.69	0.86	6.23	0.74
10	Cotton	36.74	39.28	1.14	4.87	0.50
3	Fireweed	30.72	39.81	1.28	7.12	2.06
6	Gallberry	30.15	39.85	0.72	7.71	1.22
3	Goldenrod	33.15	39.57	0.51	6.57	0.59
2	Heartsease	32.98	37.23	1.95	5.71	0.63
3	Locust, black	28.00	40.66	1.01	8.42	1.90
3	Mesquite	36.90	40.41	0.95	5.42	0.35
4	Orange, California	32.01	39.08	2.68	6.26	1.23
13	Orange, Florida	31.96	38.91	2.60	7.29	1.40
4	Raspberry	28.54	34.46	0.51	8.68	3.58
3	Sage	28.19	40.39	1.13	7.40	2.38
3	Sourwood	24.61	39.79	0.92	11.79	2.55
4	Star-thistle	31.14	36.91	2.27	6.92	2.74
8	Sweetclover	30.97	37.95	1.41	7.75	1.40
3	Sweetclover, yellow	32.81	39.22	2.93	6.63	0.97
4	Tulip tree	25.85	34.65	0.69	11.57	2.96
5	Tupelo	25.95	43.27	1.21	7.97	1.11
7	Vetch	31.67	38.33	1.34	7.23	1.83
9	Vetch, hairy	30.64	38.20	2.03	7.81	2.08
12	White clover	30.71	38.36	1.03	7.32	1.56

materials, pigments, acids, and minerals, are largely responsible for the differences among individual types.

Honey varies tremendously in color and flavor, depending largely on its floral source. Although many hundreds of kinds of honey are produced in this country, only about 25 to 30 are commercially important and are available in large quantity. These may show considerable variation in composition and properties. Until this survey of US honey was reported, the degree of variation was not known, and this retarded the use of honey by the food industry. Legume honeys—clovers and alfalfa and blends—are the most widely distributed and are available in the largest supply.

Water Content.—The water content of honey may range between 13 and 25%. According to the U.S. Standards for Grades of Extracted Honey (USDA 1951) honey may not contain more than 18.6% moisture to qualify for US grade A (US Fancy) and US grade B (US Choice). Grade C (US Standard) honey may contain up to 20% water; any higher amount places a honey in US grade D (Substandard).

These values represent limits and do not indicate the preferred or proper moisture content for honey. Honey with more than 17% moisture and a sufficient number of yeast spores will ferment. Such honey should be pasteurized, i.e., heated sufficiently to kill such organisms. This is particularly important if the honey is to be "creamed" or granulated, since this process results in a slightly higher moisture level in the liquid part. On the other hand, it is possible for honey to be too low in moisture from some points of view. In the western U.S., honey may have a moisture content as low as 13 to 14%. Such honey is somewhat difficult to handle, though it is most useful in blending with high-moisture honey to reduce its moisture content.

In the 490 samples of honey reported in the Department's Technical Bulletin 1261, the average moisture content was 17.2%. Samples ranged between 13.4 and 22.9%, the standard deviation being 1.46; thus 95.5% of all US honey will fall within the limits of 14.3 and 20.1% moisture.

Sugars.—Honey is first and foremost a carbohydrate. Sugars make up 95 to 99.9% of the solids of honey and their identity has been studied for many years. Honey was long thought to be mainly fructose and glucose, with some sucrose and "dextrins". These were considered to be poorly defined complex sugars of high molecular weight. Research in the U.S., Japan, and Canada has shown at least 11 disaccharides in honey in addition to sucrose: maltose, isomaltose, nigerose, turnanose, maltulose (White and Hoban 1959), leucrose, kojibiose (Watanabe and Aso 1960), neotrehalose, gentio-

biose, laminaribiose, and isomaltulose (Siddiqui and Furgala 1967). Most of these sugars probably do not occur in nectar, but arise because of either enzymic action during the ripening of honey or chemical action during its storage. The relative amounts of the sugars vary among individual honey types, but all types seem to have the same minor sugars.

Acids.—The acids of honey, though less than 0.5% of the solids, have a pronounced effect on the flavor. They also may be responsible in part for the excellent stability of honey against micro-organisms. At least 18 organic acids have been reported in honey, with varying degrees of certainty. Gluconic acid is now known to be the acid present in the greatest amount in honey (Stinson *et al.* 1960). Its origin will be discussed later. Other acids reported in honey are formic, acetic, butyric, lactic, oxalic, succinic, tartaric, maleic, pyroglutamic, pyruvic, α -ketoglutaric, and glycollic (Stinson *et al.* 1960).

Proteins and Amino Acids.—The nitrogen content of honey is low, on the average 0.04%, though it may range to 0.1%. Recent work has shown that only 40 to 65% of the total nitrogen in honey is protein in nature. Of the 8 to 11 proteins shown by gel electrophoresis in various honeys, 4 are common to all, and appear to originate with the bee (White and Kushnir 1967). Free amino acids, containing the remainder of the nitrogen, occur only in trace amounts, proline, glutamic acid, alanine, phenylalanine, tyrosine, leucine, and isoleucine predominating.

Minerals.—Mineral content varies from 0.02% to slightly over 1% for a floral honey, averaging about 0.17% for the 490 samples

TABLE 10.6
MINERAL CONTENT OF HONEY

Mineral	Light Honey ppm	Dark Honey ppm
Potassium	205	1,676
Chlorine	52	113
Sulfur	58	100
Calcium	49	51
Sodium	18	76
Phosphorus	35	47
Magnesium	19	35
Silica	22	36
Iron	2.4	9.4
Manganese	0.30	4.09
Copper	0.29	0.56

analyzed. Values for important minerals are shown in Table 10.6 (Schuette *et al.* 1932, 1937, 1938, 1939).

Enzymes.—One of the characteristics that distinguishes honey, at least in the unprocessed state, from all other sweetening agents is the presence of enzymes, which conceivably arise from the bee, pollen, nectar, or even yeasts and micro-organisms. Those most prominent are added by the bee in the conversion of nectar to honey. Processing and storage may reduce enzyme activities to low levels.

Invertase, added by the bee, splits sucrose into constituent sugars and produces other, more complex sugars in small percentages during this action. This in part explains the complexity of the minor sugars of honey. Although the work of invertase is completed when honey is ripened, the enzyme remains in the honey and retains its activity for some time unless inactivated by heating. Even so, the sucrose content of honey never reaches zero. Perhaps the final low value for the sucrose content of honey represents an equilibrium between hydrolysis and formation of sucrose.

Another enzyme known to be in honey is diastase (amylase). Since this enzyme digests starch to simpler compounds and starch has not been found in nectar, its function in honey is not clear. Diastase appears to be present in varying amounts in nearly all honey. Of all honey enzymes, it has probably had the greatest attention in the past, because it has been, and still is, used as a measure of honey quality (i.e. absence of damage by heating) by several European countries.

Glucose oxidase has been found in honey. This converts glucose to gluconolactone, which in turn forms gluconic acid, the principal acid in honey. Since this enzyme had previously been found in the pharyngeal gland of the honey bee, it is likely that this is the source. Here again, as with other enzymes, the percentage in different honeys is variable. In addition to gluconolactone, this enzyme forms hydrogen peroxide during its action on glucose. This has been shown to be the basis of the heat-sensitive antibacterial activity of honey (White *et al.* 1963).

Other enzymes have been reported in honey, including inulase and phosphatase. Except for catalase (Schepartz and Subers 1966) these have not been sufficiently confirmed.

Food Value

As a carbohydrate food, honey is a most delectable and enjoyable treat. Its distinctive flavors cannot be found elsewhere. The sugars are largely the easily digestible "simple sugars", similar to those of many fruits. Because of its content of such sugars, it is an excellent

source of quick energy. It can be regarded as a good food for both infants and senior citizens.

The enzymes of honey, though used as indicators of heating history and hence table quality of honey in some countries, have no nutritional value and are destroyed in the digestive process. The mineral content of honey is variable, but some darker honeys may have significant quantities of trace minerals. Although some vitamins may be demonstrated in honey, the amounts are far too low to have any meaning in human nutrition.

Granulation of Honey

Since the granulated state is natural for most of the honey produced in this country, processing is required to keep it liquid. Careful application of heat to dissolve "seed" crystals and avoidance of subsequent "seeding" will usually suffice to keep a honey liquid for 6 months. Damage to color and flavor can result from excessive or improperly applied heat. Honey that has granulated can be returned to liquid by careful heating. Heat should be applied indirectly by hot water or air, not by direct flame or high-temperature electrical source. Stirring accelerates dissolution of the crystals. For small containers, temperatures of 140° F for 30 min will usually suffice.

If unheated honey is allowed to granulate naturally, several difficulties may arise. The texture may be fine and smooth or granular and objectionable to the consumer. Furthermore, because the water content of the liquid phase increases on granulation, a granulated honey becomes more susceptible to spoilage by fermentation, caused by yeast normally found in all honeys. Quality damage from poor texture and fermented flavors is usually far greater than any caused by the heat needed to eliminate these problems.

Finely granulated honey may be prepared from a honey of proper moisture content (17.5% in summer, 18% in winter) by several processes. All involve pasteurization to eliminate fermentation, followed by addition at room temperature of 5 to 10% of a finely granulated "starter" of acceptable texture, thorough mixing, and storage at 55 to 60° F in the retail containers for about a week. The texture remains acceptable if storage is below about 80° F.

Deterioration of Honey Quality

Fermentation.—Fermentation of honey is caused by the germination and growth of yeasts normally found in all unheated honey. These yeasts, which occur naturally in honey, differ from ordinary yeasts in that they can grow at much higher sugar concentrations

than other yeasts, and are therefore called "osmophilic". Even so, there are upper limits of sugar concentration beyond which they will not grow. Thus, the water content of a honey is one of the factors concerned in spoilage by fermentation. The others are extent of contamination by yeast spores and temperature of storage.

Lochhead (1933) has written that honey with less than 17.1% water will not ferment in a year, irrespective of the yeast count. Between 17.1 and 18% moisture, honey with 1,000 yeast spores or less per gram will be safe for a year. When moisture is between 18.1 and 19%, not more than 10 yeast spores per gm can be present for safe storage. Above 19% water, honey can be expected to ferment even with only one spore per gm of honey—a level so low as to be very rare.

Martin (1958) has studied the mechanism and course of yeast fermentation in honey in his work on the hygroscopicity of honey. He confirmed that when honey absorbs moisture, which occurs when it is stored above 60% relative humidity, the moisture content at first increases mostly at the surface before the water diffuses into the bulk of the honey. In such honey, yeasts grow aerobically at the surface and multiply rapidly, whereas below the surface the growth is slower. Fermenting honey is usually at least partly granulated and is characterized by a foam or froth on the surface. It will foam considerably when heated. An odor as of sweet wine or fermenting fruit may be detected. Gas production may be so vigorous as to cause honey to overflow or burst a container.

Honey that has been slightly fermented can sometimes be reclaimed by heating it to 150°F for a short time. This stops the fermentation and expels some of the off-flavor. Fermentation in honey may be avoided by heating to kill yeasts. Minimal treatments to pasteurize honey are shown in Table 10.7 (Townsend 1939; White *et al.* 1963).

TABLE 10.7
PASTEURIZING CONDITIONS FOR HONEY

Temperature °F	Holding Time Min
128	470
130	170
135	60
140	22
145	7.5
150	2.8
155	1.0
160	0.4

Quality Loss by Heating and Storage.—The other principal types of honey spoilage—damage by overheating and by improper storage—are related. In general, changes that take place quickly during heating also occur over a longer period during storage, the rate depending on the temperature. These include darkening, loss of fresh flavor, and formation of off-flavor (caramelization).

To keep honey in its original condition of high quality and delectable flavor and fragrance is possibly the greatest responsibility of the beekeeper and honey packer. At the same time it is an operation receiving perhaps less attention from the producer than any other and one requiring careful consideration by packers and wholesalers. To do an effective job, one must know the factors that govern honey quality, as well as the effects of various beekeeping and storage practices upon it. The factors are easily determined, but only recently are the facts regarding the effects of processing temperatures and storage on honey quality becoming known.

The objective of all processing of honey is simple—to stabilize it, that is, to keep it free of fermentation and to maintain the desired physical state, be it liquid or finely granulated. Methods for accomplishing these objectives have been fairly well worked out and have been used for many years. Probably improvements can be made. The requirements for stability of honey are more stringent now than in the past, since honey is a world commodity, available in supermarkets the year around. Government price support and loan operations require storage of honey, and market conditions may also require storage at any point in the handling chain, including the producer, packer, wholesaler, and exporter.

Application and control of heat is the primary operation in the processing of honey. If we consider storage to be the application of or exposure to low amounts of heat over long periods, it can be seen that a study of the effects of heat on honey quality can have a wide application.

Any assessment of honey quality must include flavor considerations. The objective measurement of changes in flavor, particularly where they are gradual, is most difficult.

As indicators of the acceptability of honey for table use, Europeans have for many years used the activity of certain enzymes and the content of hydroxymethylfurfural (HMF) in honey. They consider that heating honey sufficiently to destroy or greatly lower its enzyme content reduces its desirability for most uses; HMF level is also a measure of heat exposure. A considerable difference has been noted in reports by various workers on the sensitivity to heat of enzymes, largely diastase and invertase, in honey. It is now known that storage alone is sufficient to reduce enzyme content and

produce HMF in honey (White *et al.* 1963). Since some honey types frequently exported to Europe are naturally low in diastase, the response of diastase and invertase to storage and processing is of great importance for exporters.

The Codex Alimentarius standards for honey (Codex Alimentarius Commission 1969) require certain combinations of HMF content and diastase activity, depending upon honey type. Because US authorities and honey producers and packers do not agree with the use of HMF and diastase levels as quality indicators, the Codex honey standards have not been accepted in the U.S.

A study of the effects of heating and storage on honey quality was based on the results with three types of honey stored at six temperatures for two years (White *et al.* 1963). The results were used to obtain predictions of the quality life of honey under any storage conditions.

The damage done to honey by heating and by storage is the same. For lower storage temperatures, a much longer time is required to obtain the same result. It must be remembered that the effects of processing and storage are additive. It is for this reason that proper storage is so important. A few periods of hot weather can offset the benefits of months of cool storage: 10 days at 90° F are equivalent to 100 to 120 days at 70° F. An hour at 145° F in processing will cause changes equivalent to 40 days' storage at 77° F.

For storing honey, conditions must be selected that will minimize fermentation, undesirable granulation, and heat damage. Fermentation is strongly retarded below 50° F and above 100° F. Granulation is accelerated between 55° and 60° F and may be initiated by fluctuation at 50° to 55° F. The best condition for storing unpasteurized honey would seem to be below 50° F, or winter temperatures over much of the United States. Warming above this range in the spring can initiate active fermentation in such honey, which is usually granulated and thus even more susceptible.

Some progressive producers and packers are now using controlled temperature storage for honey, particularly in the warmer regions. Using the data from the storage study noted above, we can definitely state that lowering the storage temperature of honey by 10 to 15° F will reduce the rate of deterioration to about one-third to one-sixth of that at the higher temperature. Such a temperature reduction would reduce HMF production to one-third, enzyme loss to one-fifth to one-sixth, and darkening rate to about one-sixth of the rate at the higher temperature. Loss of flavor and freshness would be expected to be reduced similarly. Thus, honey can at any time of the year be more nearly like honey at its very best—fresh from the comb at extraction time.

Marketing and Use

A large part of the honey sold to consumers in the U.S. is in the liquid form, much less in a finely granulated form known as "honey spread" or finely granulated honey, and even less as comb honey. The consumer appears to be conditioned to buying liquid honey, since sales of the more convenient spread form have never approached those of liquid honey. Comb honey has nearly disappeared, though "chunk comb" or comb immersed in liquid honey is sometimes seen in the market. Bulk honey is usually available in 55-gal drums, and tank-truck handling has been reported.

Most industrial use of honey is in baking and other food manufacturing, and in nonprescription cough syrups and tablets. The high fructose content and desirable flavors generally provide customer satisfaction in its uses. It is used in breakfast cereals, syrups, confections, cured meat products, and fruit juices to add a note of "old-fashioned goodness" sought by many customers. It is an optional ingredient for jams, jellies, and preserves.

Several dry products for food manufacture containing a high proportion of honey are commercially available. A pure dry honey product and one containing up to one-third sucrose have been described, but are not in commercial production (Turkot *et al.* 1960). Commercially available materials include Honi-Bake® (Glabe *et al.* 1963) which contains about 23% gelatinized starch. Dry combinations of milk and honey have been described (Walton *et al.* 1951; Webb and Walton 1952; Torr 1966, 1967) but are not commercially available.

Information is available on the use of honey in the manufacture of breads (Smith and Johnson 1951), cake and sweet doughs (Smith and Johnson 1952), cookies (Smith and Johnson 1953A), fruit cake (Smith and Johnson 1953B), and it is a vehicle in medicinal preparations (Rubin *et al.* 1959).

In conclusion, although these two minor sweetening agents, maple syrup and honey, are available in far less quantity than the major sweeteners, their delectable flavors and the unique nature of their origins keep the discerning consumer and creative food technologist interested in using them whenever possible.

BIBLIOGRAPHY

- CODEX ALIMENTARIUS COMMISSION, FAO/WHO. 1969. Recommended European regional standards for honey. CAC/RS 12-1969. 23 pp.
- CONNELLY, J. A. 1969. Two automatic syrup drawoff controllers. USDA, Agr. Res. Service, ARS 73-60. Washington, D.C. 12 pp.
- EDSON, H. A., JONES, C. H., and CARPENTER, C. W. 1912. Microorganisms of maple sap. Vt. Agr. Expt. Sta. Bull. 167, [321] 610.

- FILIPIC, V. J., UNDERWOOD, J. C., and DOOLEY, C. J. 1969. Trace components of the flavor fraction of maple syrup. *J. Food Sci.* 34, 105-110.
- FOX, W. F., and HUBBARD, W. F. 1905. The maple sugar industry. Bulletin No. 59. USDA, Bureau Forestry, Washington, D.C.
- GLABE, E. F., GOLDMAN, P. F., and ANDERSON, P. W. 1963. Honey solids—a new functional sweetener for baking. *Bakers' Digest* 37, (5), 49-50, 52-54.
- HART, F. L., and FISHER, H. J. 1971. *Modern food analysis*. Springer-Verlag, New York.
- HAYWARD, F. W., and PEDERSON, C. S. 1946. Some factors causing dark-colored maple syrup. *N.Y. State Agr. Expt. Sta. Bull.* 718, 14 pp. illus.
- HOMEMAKERS GUILD OF AMERICA. 1961. A consumer survey on flavored syrups; conducted for Owens-Illinois, Toledo, Ohio.
- LOCHHEAD, A. G. 1933. Factors concerned with the fermentation of honey. *Zentr. Bakteriell. Parasitenk.* II Abt. 88, 296-302.
- MARTIN, E. C. 1958. Some aspects of hygroscopic properties and fermentation of honey. *Bee World* 39, 165-178.
- NEARING, H., and NEARING, S. 1950. *The maple sugar book*. The John Day Co., New York.
- RAYMOND, LYLE S., JR., and WINCH, FRED E., JR. 1959. *Maple syrup production in New York State*. N.Y. State Col. and Agr., Cornell U., Ithaca, N.Y. 2nd ed., rev.
- RUBIN, N., GENNARO, A. R., SIDERI, C. N., and OSOL, A. 1959. Honey as a vehicle for medicinal preparations. *Am. J. Pharm.* 131, 246-254.
- SCHEPARTZ, A. I., and SUBERS, M. H. 1966. Catalase in honey. *J. Apicult. Res.* 5, 37-43.
- SCHUETTE, H. A., and REMY, K. 1932. Degree of pigmentation and its probable relationship to the mineral constituents of honey. *J. Am. Chem. Soc.* 54, 2909-2913.
- SCHUETTE, H. A., and HUENINK, D. J. 1937. Mineral constituents of honey. II. Phosphorus, calcium, magnesium. *Food Res.* 2, 529-538.
- SCHUETTE, H. A., and TRILLER, R. E. 1938. Mineral constituents of honey. III. Sulfur and chloride. *Food Res.* 3, 543-547.
- SCHUETTE, H. A., and WOESSNER, W. W. 1939. Mineral constituents of honey. IV. Sodium and potassium. *Food Res.* 4, 349-353.
- SIDDIQUI, I. R., and FURGALA, B. 1967. Isolation and characterization of oligosaccharides from honey. I. Disaccharides. *J. Apicult. Res.* 6, 139-145.
- SMITH, L. B., and JOHNSON, J. A. 1951. The use of honey in bread products. *Bakers' Dig.* 25 (6), 103-106.
- SMITH, L. B., and JOHNSON, J. A. 1952. The use of honey in cake and sweet doughs. *Bakers' Dig.* 26 (6), 113-118.
- SMITH, L. B., and JOHNSON, J. A. 1953A. Honey—its value and use in popular cookies. *Bakers' Dig.* 27 (2), 28-31.
- SMITH, L. B., and JOHNSON, J. A. 1953B. Honey improves fruit cake quality. *Bakers' Dig.* 27 (3), 52-54.
- STINSON, E. E., SUBERS, M. H., PETTY, J., and WHITE, J. W., JR. 1960. The composition of honey. V. Separation and identification of the organic acids. *Arch. Biochem. Biophys.* 89, 6-12.
- STROLLE, E. O., CORDING, J., JR., and ESKEW, R. K. 1956. An analysis of the open-pan maple syrup evaporator. USDA, Agr. Res. Service, ARS 73-14. Washington, D.C. 14 pp.
- TORR, D. 1966. Dried honey-milk product. U.S. Patent 3,244,528 April.
- TORR, D. 1967. Dried honey-milk product. U.S. Patent 3,357,839 December.
- TOWNSEND, G. F. 1939. Time and temperature in relation to the destruction of sugar-tolerant yeasts in honey. *J. Econ. Entomol.* 32, 650-654.
- TURKOT, V. A., ESKEW, R. K., and CLAFFEY, J. B. 1960. A continuous process for dehydrating honey. *Food Technol.* 14, 387-390.
- UNDERWOOD, J. C. 1971. Effect of heat on the flavoring components of maple syrup. *J. Food Sci.* 36, 228-230.

- UNDERWOOD, J. C., and WILLITS, C. O. 1963. Research modernizes the maple syrup industry. *Food Technol.* 17, 1380-1382, 1384-1385.
- U.S. DEPT. AGR., AGR. MKTG. SERVICE. 1940. United States standards for grades of table maple syrup. Washington, D.C.
- U.S. DEPT. AGR., AGR. MKTG. SERVICE. 1951. United States standards for grades of extracted honey. Washington, D.C. 6 pp.
- U.S. DEPT. AGR. 1972. *Agricultural Statistics*. Washington, D.C. 117.
- WALTON, G. P., WHITE, J. W., JR., WEBB, B. H., HUFNAGEL, C. F., and STEVENS, A. H. 1951. Manufacture of concentrated milk and honey products. *Food Technol.* 5, 203-207.
- WATANABE, T., and ASO, K. 1960. Studies on honey. II. Isolation of kojibiose, nigerose, maltose, and isomaltose from honey. *Tohoku J. Agr. Res.* 11, 109-115.
- WEBB, B. H., and WALTON, G. P. 1952. Dried honey-milk product. U.S. Patent 2,621,128. December.
- WHITE, J. W., JR., and HOBAN, N. 1959. Composition of honey. IV. Identification of the disaccharides. *Arch. Biochem. Biophys.* 80, 386-392.
- WHITE, J. W., JR., RIETHOF, M. L., SUBERS, M. H., and KUSHNIR, I. 1962. Composition of American honeys. U.S. Dept. Agr., Tech. Bull. 1261. Washington, D.C. 1-124.
- WHITE, J. W., JR., KUSHNIR, I., and SUBERS, M. H. 1963. Effect of storage and processing temperatures on honey quality. *Food Technol.* 18, 555-558.
- WHITE, J. W., JR., SUBERS, M. H., and KUSHNIR, I. 1963. How processing and storage affect honey quality. *Gleanings in Bee Cult.* 91, 422-425.
- WHITE, J. W., JR., SUBERS, M. H., and SCHEPARTZ, A. I. 1963. The identification of inhibine, the antibacterial factor in honey, as hydrogen peroxide and its origin in a honey glucose-oxidase system. *Biochem. Biophys. Acta* 73, 57-70.
- WHITE, J. W., JR., and KUSHNIR, I. 1967. Composition of honey. VII. Proteins. *J. Apicult. Res.* 6, 163-178.
- WILLITS, C. O. 1965. *Maple syrup producers manual*. USDA, Agr. Handbook No. 134, Rev., Washington, D.C.